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LET effects on the hydrogen production induced by the radiolysis of pure water.

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Abstract

Radiation chemical primary yields $g(H_2)$ have been determined for irradiations performed with ^{60}Co γ -rays source of LCP (Orsay, France) and with helium ions beams ($E_\alpha = 5.0$ MeV to 64.7 MeV) using protective agent bromide anions in solution. The α ($^4He^{2+}$) irradiation experiments were performed either at CEMHTI or at the new ARRONAX cyclotron facility (2010). Both sources (γ and cyclotrons) allow working with a large LET value range between 0.23 to 151.5 keV/ μm . On one hand, the obtained results have been compared with those available in the literature and plotted as a function of the LET parameter in order to discuss the effects of track structure on the production of molecular hydrogen. On the other hand, the primary radiation chemistry yield $g(H_2)$ values are compared with global radiation chemical yields $G(H_2)$ obtained during irradiations of pure water irradiated under air or argon without scavenging. For each system, it appears that radiation chemical yields increase with the LET value. Our results suggest that using bromide anions, at low concentration, as a protective agent becomes ineffective when the LET value used is higher than 120 ± 20 keV/ μm .

Keywords

Gamma irradiation, Alpha irradiation, Water radiolysis, LET parameter, Molecular hydrogen radiation chemical yield, scavenging efficiency.

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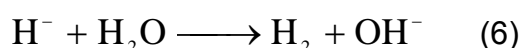
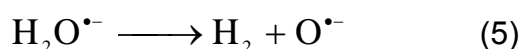
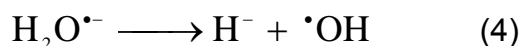
1. Introduction

Molecular hydrogen is one of the main species produced by the radiolysis of water and its chemistry has been studied extensively (BUXTON, 2004; HOCHANADEL, 1952; LAVERNE et al., 2009; LAVERNE, 2000; PASTINA, 2001). Indeed, applications in the accurate measurements of the radiation chemical H_2 yields.

Many studies on the radiolysis of water have mentioned different possibilities of precursors and mechanisms for the formation of the molecular hydrogen (BYAKOV, 1976; DOMAE et al., 1996; FARAGGI, 1973; FARAGGI and DESALOS, 1969; GHORMLEY and HOCHANADEL, 1954; HAMILL, 1969; HAYON and MOREAU, 1965; HOCHANADEL, 1952; MAHLMAN, 1963; PASTINA, 1999; PELED, 1969; SCHWARZ, 1955; SCHWARZ, 1969; SCHWARZ et al., 1954). According to the literature, the three following reactions are considered responsible for the majority of the formation of molecular hydrogen (Buxton et al., 1988).



Others mechanisms are given in the literature to explain the production of molecular hydrogen. Among them, the dissociation of excited water molecules to give O atoms and molecular hydrogen (Slanger and Black, 1982), the capture of precursors to the hydrated electron by a water (Cobut et al., 1996; Faraggi et al., 1971; Goulet and Jay-Gerin, 1989) in order to obtain a molecular anion which may decompose itself to give molecular hydrogen directly or produce an hydride anion that produces molecular hydrogen as shown in the following reactions :



This statement is true for irradiation with low LET values. However, when irradiations are performed with high LET values, other mechanisms have been proposed in the literature (LAVERNE, 2000). Indeed, authors have shown that a dissociative recombination between a molecular water cations and electron that are formed in

close proximity after the irradiation will not diffuse but react quickly each other in order to form molecular hydrogen.

In the first radiation chemistry experiments of water, a low concentration of molecular hydrogen (Hochanadel, 1952) was measured induced by its consumption by others species created during the radiolysis of the water. In order to measure the radiation chemistry primary yield of molecular hydrogen, $g(H_2)$, different chemical systems using scavengers or protective agents are proposed in the literature: among them, a solution of $10^{-3}M$ bromide ions irradiated under desaerated conditions (Allen, 1961), a system using a cerium dosimeter ($3 \cdot 10^{-5}M$ Ce(IV) / $10^{-5}M$ Ce(III)) irradiated under argon (Ferradini and Pucheault, 1983) and a $2 \cdot 10^{-3}M$ nitrite ion solution irradiated under deaerated conditions (Sunaryo et al., 1994). For each of these systems irradiated using a ^{60}Co γ -source at room temperature, the primary yield of molecular hydrogen was determined at 0.45 ± 0.03 molecules/100 eV by several works in the literature (ALLEN, 1961; DRAGANIC et al., 1969; FARAGGI, 1973; FERRADINI and PUCHEAULT, 1983; ISHIGURE et al., 1995; LA VERNE, 1989; LAVERNE, 2002; LAVERNE, 2003; LAVERNE, 2005; PASTINA, 2001; PASTINA, 1999; PELED, 1969; SCHWARZ, 1955; SUNARYO et al., 1994).

Furthermore, there are few different works (ANDERSON and HART, 1961; APPLEBY and SCHWARZ, 1969; PASTINA, 2001) on the production of molecular hydrogen using other particles with higher Linear Energy Transfer ($LET = -dE/dx$) than γ -rays. It appears that when the LET value increases, the density of radicals increases in the ionization tracks. So the radicals have a higher probability to combine each others than to diffuse from the spurs in which they are formed (Allen, 1961). It ensues from this fact that with high LET radiations, the radical yields decrease whereas the molecular product yields increase due to the radical-radical reactions. Indeed, it was a very interesting topic to understand the evolution of radiation chemical yields as a function of the LET value.

One of the first experiments using α -particles was performed in (Schuler and Allen, 1957). Authors worked on the irradiation of a Fricke dosimeter solution using cyclotron beams of helium (34.5 MeV (37.3 keV/ μm) and 21.8 MeV (53 keV/ μm)) or proton (18 MeV, 5 keV/ μm) and determined $G(H_2)$ values of 1.06, 1.18 and 0.82 molecules /100 eV, respectively. Then, experiments using ^{210}Po in water (Lefort and Tarrago, 1959) (~ 5 MeV, ~ 130 keV/ μm) were performed to observe the quantity of

molecular hydrogen formed by ^{210}Po radiation. The $G(\text{H}_2)$ value given in this work is 1.57 molecules/100eV. In (ANDERSON and HART, 1961), new experiments determined the molecular and radical products in the radiolysis of water using proton and helium ion beams of different energies. In this work, the radiation chemical yield of molecular hydrogen varies from 0.60 molecules/100 eV using proton beams to 1.29 molecules/100 eV using alpha particle beams. Then in (Appleby and Schwarz, 1969), primary radiation chemical yields of molecular hydrogen, $g(\text{H}_2)$, were measured using 18 MeV deuteron (9 keV/ μm) and 12 and 32 MeV (83 keV/ μm and 40 keV/ μm) helium ions beams. The $g(\text{H}_2)$ values obtained were 0.68, 1.11 and 0.96 molecules/100eV, respectively. Later, a new investigation (Pastina, 2001) on the effect of molecular hydrogen on hydrogen peroxide in the water radiolysis needed to get informations on the $g(\text{H}_2)$ value vs. the LET parameter. In this work, the authors obtained $g(\text{H}_2)$ values for 10 MeV (13.8 keV/ μm) and 2 MeV (34.8 keV/ μm) proton beams and 5 MeV helium ion beams (151.5 keV/ μm) and the yields of molecular hydrogen were 0.64, 0.90 and 1.20 respectively.

This short review shows that the radiation chemical yield of H_2 value is strongly dependent on the LET value and is worthy of measuring more accurately on a large range. That is the reason why, in order to enhance the understanding about the scavenging effect on molecular hydrogen production, we propose to study the scavenging effect parameter on a large LET value range (from 0.23 to 151.5 keV/ μm). Then, the main purpose of these experiments is to show the difference on the radiation chemical yield of hydrogen molecular observed between ultrapure water irradiated with or without scavengers in order to determine the LET range of the scavenging efficiency. Moreover, use of the ARRONAX cyclotron facility aids in enhancing our knowledge of this topic because its characteristics (up to 68 MeV helium ion beams) allow working with new LET values for $^4\text{He}^{2+}$ ions particle beam hitherto not available in the literature.

2. Experimental

The irradiated solutions were made with sodium bromide (NaBr , ACS reagent grade, Aldrich), sodium nitrite (NaNO_2 , ACS reagent grade, Aldrich) and cerium sulfate ($\text{Ce}(\text{SO}_4)_2$, Aldrich). The solutions were prepared using water from a Millipore

Milli-Q UV system. Most of the solutions were saturated with ultrahigh purity Ar (99.9999 %).

Irradiations with γ -rays were performed using a panoramic ^{60}Co source at the Laboratoire de Chimie-Physique (LCP, Orsay, France). The dose rate was about 1100 Gy/h as determined using the Fricke Dosimeter with a radiolytic yield $G(\text{Fe}^{3+})$ equal to 15.6 molecules/100eV. The cells used for the irradiations are in PEEK and the volume of irradiated solution was 20 ml. The samples were stirred sufficiently to consider a homogenous solution during all the experiments.

Ions beams of $^4\text{He}^{2+}$ were provided by the CEMHTI cyclotron (Orléans, France) and the new cyclotron ARRONAX (St Herblain, France). The CEMHTI cyclotron generates alpha particle beams with energies of 28 MeV or 45 MeV. The cells used are the same than for the γ irradiation and the thickness of the glass window, which allows the passage of the particles, varied between 150 μm (38.7 mg/cm^2) and 450 μm (116.1 mg/cm^2). Calculations using the SRIM2008 code gave energy ranges from 5.0 to 22.5 MeV inside the sample using the CEMHTI facility (ZIEGLER et al., 1985; ZIEGLER et al., 2010). The energies of the particles used during our experiments are too low to irradiate the entire thickness of the cells. The ions are totally stopped in the solution and the values of integral LET are between 38.8 $\text{keV}/\mu\text{m}$ and 151.5 $\text{keV}/\mu\text{m}$. The ARRONAX cyclotron facility provides a $^4\text{He}^{2+}$ ion beam of 68.4 MeV with a diameter of 10 mm. In this geometry, the energy deposited in our sample is 64.7 MeV and the integral LET is 22.7 $\text{keV}/\mu\text{m}$. In order to be able to work with helium ion beams of different energies, we have to use foils of titanium with different thicknesses (500-700 μm or 225-315 mg/cm^2). The energies obtained in our cells are 39.5 and 27.6 MeV and the associated integral LET are 33.8 and 36.5 $\text{keV}/\mu\text{m}$. During all the experiments, the current value of $^4\text{He}^{2+}$ flux in solution is fixed at 70 nA. Providing by the CEMHTI cyclotron, the flux of $^4\text{He}^{2+}$ particles within the irradiation cell is measured with a Faraday cup and set to 70 nA depending on the experiment. The stability of the $^4\text{He}^{2+}$ ions beam was checked by monitoring the beam current set down in an ionization chamber located upstream to the irradiation cell. Other experiments are carried out within ARRONAX cyclotron. The intensity of the particles beam, measured on an internal Faraday cup located one meter upstream, is maintained at 70 nA. The uncertainty of that current measurement is of 10 %. Fricke dosimetry (FRICKE and HART, 1966) is used in this study in order to determine the

dose deposited into the samples. This method is based on the oxidation of Fe^{2+} to Fe^{3+} by the species produced by the water radiolysis reactions. The concentration of ferric ions is monitored by UV-Vis measurements at 304 nm ($\epsilon = 2197 \text{ L.mol}^{-1}.\text{cm}^{-1}$, 298 K) with a spectrophotometer CARY4000 (VARIAN). These measurements are carried out on samplings few minutes after irradiation onto the CEMHTI beam-line or during the irradiation onto the ARRONAX beam-line. Super Fricke solutions are prepared by dissolving the desired quantity of Mohr's salt ($[\text{Fe}^{2+}] = 10 \text{ mmol.L}^{-1}$) and NaCl (1 mmol.L^{-1}) in aerated aqueous $0.4 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ solutions. All reagents are analytical grade or equivalent. NaCl is added in order to avoid any organic impurities. The Fricke dose rates for the irradiation are in the range from 1.5 to 3 kGy/min using the ferric ion radiolytic yield coming from the literature (LAVERNE and SCHULER, 1987; MATSUI et al., 1970; SAINI and BHATTACHARYYA, 1987).

Molecular hydrogen is measured with a gas chromatograph. Ultra high purity argon is used as the carrier gas. The gas chromatograph is a 490-GC, which is a μ -GC model from VARIAN. Both injection and μ -GC systems are Argon-purged before each measurement. The gas sample is introduced at atmospheric pressure in an injection loop which volume is 10 μl . Then, gas is compressed at 150 kPa in the column that is a Molecular Sieve 5A ($L \sim 4\text{m}$, $\varnothing \sim 0.25 \text{ mm}$). The detection is performed using a thermal conductivity detector. Calibration of the detector is performed by injection of different gas mixtures of hydrogen in argon from 10 to 500 ppm hydrogen in the composition of the gas. Error in gas measurements is estimated to be less than 10%.

3. Results and discussion

3.1. Chemical scavenging system validation

Many results on the hydrogen molecular primary yield are suggested in the literature using γ -irradiation. In these works, the authors used different chemical systems to measure $g(\text{H}_2)$ values. Among them, solutions of 1 mM NaBr irradiated under argon, solutions of 1 mM NaNO_2 irradiated under argon, and a solution of cerium sulfate dosimeter irradiated under air have been studied.

The results presented in this work show the differences between these three systems and the corresponding measured numerical yields are given in the Table 1. This table shows that we obtain the well-known value of $g(\text{H}_2) = 0.45 \text{ molecules/100eV}$ (± 0.05

molecules/100eV) using a solution of 1 mM NaBr irradiated under argon saturated conditions which is not the case for the other systems. Thus, this chemical system will be used in this work to obtain the $g(H_2)$ values in the following set of experiments.

3.2. Comparison between $g(H_2)$ and $G(H_2)$ under γ - irradiation

The yields of molecular hydrogen produced by γ -irradiation of ultrapure water under air or argon are shown in Figure 1. Also shown is the yield value found for a solution of 10^{-3} M NaBr irradiated under argon saturated conditions allowed elucidation of the primary radiation chemical yield of molecular hydrogen. It is validated that the production of molecular hydrogen is proportional to the dose deposited into the solution for each system. Moreover, the yield values measured for ultrapure water irradiated under air or argon saturated conditions give almost the same value of $G(H_2)$, $0.25 (\pm 0.03)$ and $0.28 (\pm 0.03)$ molecules/100eV, respectively. These values are in agreement with the results obtained by (ESSEHLI et al., 2011) using the same system. However, the addition of NaBr in water gives a $g(H_2)$ -value which is much higher (0.45 molecules/100eV). This result can be explained by the scavenging of hydroxyl radicals by bromide ions as shown by (LAVERNE et al., 2009). Indeed, the reaction between HO^\bullet radicals and H_2 is suppressed due to the competition between the following reactions:



The obtained result leads to a higher production of molecular hydrogen than with pure water because reaction 8 is widely favored due to the concentration of bromide ions (10^{-3} M) used in our experiment that are in at a sufficiently high enough concentration to scavenge the HO^\bullet radicals.

3.3. Evolution of $g(H_2)$ vs. LET value

Molecular hydrogen production according to the LET values (0.23 keV/ μ m to 151.5 keV/ μ m) is monitored using three different sources of irradiation: γ -rays and helium ion beams of two different facilities, CEMHTI cyclotron (Orléans, France) and the new ARRONAX cyclotron (Saint-Herblain, France). The numerical values of radiation chemical primary yields $g(H_2)$ obtained irradiating a sodium bromide solution varied from $0.45 (\pm 0.05)$ to $1.20 (\pm 0.12)$ molecules/100eV and are presented in Table 2.

Molecular hydrogen yield increases with increasing LET value. Indeed, the density of initial radicals produced in the track increases with the LET as well as the frequency of intra-track reactions. This result can be explained by the “tracks theory” presented by (MAGEE and CHATTERJEE, 1987).

Moreover, previous reports have provided primary g-values of H₂ at different LET (ANDERSON and HART, 1961; APPLEBY and SCHWARZ, 1969; PASTINA, 2001) and our present experimental results are compared with these reported values. Figure 2 shows the evolution of g(H₂) plotted as a function of the LET value. The g(H₂) values of our present work are in agreement with pre-quoted reports. In addition, we obtained new values of g(H₂) with ⁴He²⁺ ion beams using the new cyclotron at ARRONAX. Indeed, the characteristics of the ion beam provided by this facility (64.7 MeV in our sample) allow us to work with lowest LET value (22.7 keV/μm) for helium ion beams.

3.4. Evolution of G(H₂) vs. LET value

In this section, we observed the effects of the atmosphere used in our sample on molecular hydrogen production as a function of the LET during the radiolysis of pure water. Two different atmospheric conditions are observed during our experiments: aerated conditions and argon-saturated conditions. The numerical values of radiation chemical yields, G(H₂), obtained varied from 0.25 (± 0.03) to 1.30 (± 0.13) molecules/100eV, are presented in Table 3 and are plotted with regard to the LET in Figure 3.

The results show that the G(H₂) values increase for both systems (aerated and argon-saturated water) when the LET become higher as it was observed for a bromide solution. Again, this result is due to the “track theory” enounced by (MAGEE and CHATTERJEE, 1987). Moreover, there is no observable difference in yields between argon-saturated water and aerated water. This result could be questionable because we know that molecular oxygen, O₂, is a good scavenger of hydrated electrons, e⁻_{aq}, as described below in reaction (9):



Indeed, we know that the hydrated electron is responsible for the most part in the formation of molecular hydrogen (see reactions (2) and (3)). Therefore, if it is

scavenged by O_2 , the production of molecular hydrogen in the aerated system should be lower than in the argon-saturated system but this is not the case. This result can be explained by the quite low concentration ($2.8 \cdot 10^{-4}$ M) of oxygen dissolved in water, where this value is calculated using the Winkler method table at room temperature (20°C). In these conditions, the scavenging of the hydrated electron by the oxygen is too slow to be effective because it occurs when the homogeneous conditions had been already started. Moreover, the low concentration of superoxide radicals, HO_2^\bullet (0.06 molecules/100eV for a LET-value of $250 \text{ keV}/\mu\text{m}$) (BALDACCHINO et al., 1998; BALDACCHINO et al., 2001) confirms that the HO_2^\bullet / electron reaction can be considered as negligible in our conditions because the $G(HO_2^\bullet)$ increases with the LET so it is lower than 0.06 molecules/100eV in our works.

3.5. Comparison between $g(H_2)$ and $G(H_2)$ with the LET

Figure 3 shows the variation of the radiation chemical yields of molecular hydrogen for our different systems in the same graphic. It can be seen following interpolations (dashed lines) that the production of H_2 is different with the LET between ultrapure water systems or bromide sodium solutions system. Indeed, it seems that for LET values lower than about $120 \text{ keV}/\mu\text{m}$ ($\pm 20 \text{ keV}/\mu\text{m}$), the radiation chemical primary yields of molecular hydrogen, $g(H_2)$, are higher than those obtained for ultrapure water systems, $G(H_2)$, for a given LET value. This result can be explained, as mentioned above, by the suppression of reaction (7) and enhancement of reaction (8). In this case, the formation of H_2 is protected by the scavenging of hydroxyl radicals using bromide ions. However, when the LET becomes higher than $120 \text{ keV}/\mu\text{m}$, we can observe a quite different behavior of the evolution of the two interpolation curves. For these LET values, it can be observed that $G(H_2)$ is approximately equal to the $g(H_2)$. This result is rather unexpected since it means that the presence of the bromide ions in our sample does not affect the radiation chemical yield values of molecular hydrogen. Consequently, the scavenging of HO^\bullet radicals by the halide is not significant enough to show differences between systems containing bromide ions or not. A possible explanation of this phenomenon can be given by the distribution of the heterogeneities in the solution. If the LET increases the spurs tend to be closer to one another. In this case, the probability of a combination of radicals is largely higher than their diffusion from the spurs in which they are formed. Thus, the concentration of radicals in the water becomes much lower than has been shown in

the literature (PASTINA, 2001). Indeed, $G(\text{HO}^\bullet)$ is 0.35 molecules/100 eV using $^4\text{He}^{2+}$ beam of 5 MeV (151.5 keV/ μm) whereas this value is equal to 2.70 molecules/100 eV using γ -rays. Therefore, reactions (7) and (8) have a weaker role when the LET is high because the concentration of radical hydroxyls are much lower in these conditions than under low LET irradiation conditions. These results clearly highlight that the presence of scavengers, during irradiations occur using high LET particles, is not necessary because the concentration of HO^\bullet radicals is too low to have an impact on the production of hydrogen. Moreover, a similar result has been shown by (ESSEHLI et al., 2011) in the literature using TiO_2 anatase particles in solution. Indeed, it had been shown that TiO_2 particles have a scavenging role vs. the HO^\bullet radical. The radiation chemical yields of H_2 measured for a TiO_2 suspension in pure water using γ -ray irradiation gave 0.41 molecules/100 eV whereas this value is equal to 0.30 molecules/100 eV without TiO_2 particles in water. However, when these systems had been irradiated using a $^4\text{He}^{2+}$ ion beam of 5 MeV, the radiation chemical yields obtained for both was 1.25 molecules/100 eV. Again, this result shows that the concentration of HO^\bullet radicals escaping the track is too low at high LET values to be clearly involved in the consumption of molecular hydrogen. Also, (PASTINA, 2001) have shown that the scavenging of HO^\bullet radicals by the addition of H_2 is only efficient using low LET ions such as 2 or 10 MeV protons. The authors have proposed that the production of hydrogen peroxide decreases with regard to the same experiment realized without an addition of H_2 for the same dose. However, when the authors worked with higher LET particles, such as 5 MeV helium ions beams, they proposed a different conclusion. Indeed, an addition of H_2 does not change anything on the production of H_2O_2 . This result is in agreement with our discussion because in both cases reaction (7) is involved and the concentration of HO^\bullet escaping the track is too low to influence the consumption of H_2 whatever the system in this present paper or in the one relative to the formation of H_2O_2 .

4. Conclusion

The radiolysis of water using bromide ions as scavengers of radical hydroxyls shows differences on the production of molecular hydrogen under γ -rays irradiation with regard to the radiolysis of pure water. The radiation chemical primary yield $g(\text{H}_2)$ is found to be higher than $G(\text{H}_2)$ obtained without a protective agent as already

established in the literature. Moreover, there is no difference clearly observed on production of H₂ between irradiations under argon-saturated conditions or aerated conditions which confirms the negligible scavenging effect of the oxygen in this LET range due to its low concentration in solution. The radiation chemical yield of molecular hydrogen increases according to the LET for each solution observed in this work as shown in the literature. However, irradiations using high LET particles, up to 120 keV/μm, show no difference between systems containing scavengers or without the presence of scavengers. Then, we have established the efficiency range of the bromide ions scavenging (at low concentration) vs. the hydrogen production between 0 and 120 ± 20 keV/μm for the LET values. This phenomenon is explained by the very low concentration of radical escape in pure water in these conditions. Further experiments on the production of H₂ using a “constant” LET in our cells are in progress. These results will be presented with different applications of Monte Carlo track codes.

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